Synthesis and characterization of manganese(IV) and ruthenium(III) complexes derived from bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone

Mahesh K. Singh [a]; Nirmal K. Kar [a]; Ram A. Lal [b]

[a] Department of Chemistry, Tripura University, Suryamaninagar-799130, Tripura, India [b] Department of Chemistry, North-Eastern Hill University, Shillong-793022, Meghalaya, India

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Synthesis and characterization of manganese(IV) and ruthenium(III) complexes derived from *bis*(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone

MAHESH K. SINGH*†, NIRMAL K. KAR† and RAM A. LAL‡

†Department of Chemistry, Tripura University, Suryamaninagar – 799130,
Tripura, India
‡Department of Chemistry, North-Eastern Hill University,
Shillong – 793022, Meghalaya, India

Bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone(naohH$_4$) interacts with manganese(II) acetate in methanol followed by addition of KOH giving [Mn^{IV}(naoh)(H$_2$O)$_2$]. Activated ruthenium(III) chloride reacts with naohH$_4$ in methanol yielding [Ru^{III}(naohH$_4$)Cl(H$_2$O)Cl$_2$]. The replacement of aquo by heterocyclic nitrogen donor in these complexes has been observed when the reaction is carried out in presence of heterocyclic nitrogen donors such as pyridine(py), 3-picoline(3-pic) or 4-picoline(4-pic). The molar conductance values in DMF for these complexes suggest non-electrolytic nature. Magnetic moment values suggest +4 oxidation state for manganese in its complexes, however, ruthenium(III) complexes are paramagnetic with one unpaired electron. Electronic spectral studies suggest six coordinate metal ions. IR spectra reveal that naohH$_4$ coordinates in enol-form and keto-form to manganese and ruthenium, respectively. ESR and cyclic voltammetric studies of the complexes have also been reported.

Keywords: Manganese(IV); Ruthenium(III); Bis(2-hydroxy-1-naphtaldehyde)oxaloyldihydrazone

1. Introduction

Several important roles are being played by manganese in biological systems [1, 2]. Among these, manganese in the photosystem-II is of particular interest, where manganese in higher oxidation state functions as a catalyst for oxidizing water to molecular oxygen [3]. It is believed that manganese(II) is raised to higher oxidation states Mn(III) and Mn(IV). All these forms of manganese protein complex are involved. While EXAFS studies indicate that only N and O donor atom are bound to manganese, there is no evidence for a manganoporphyrin center in the oxygen evolving complex (OEC) [2]. In the catalase isolated from *lactobacillusplantarum*, the existence of binuclear manganese has also been proposed [4]. The coordination chemistry of

*Corresponding author. Email: maheshkumar_singh@rediffmail.com

manganese is dominated by stable Mn(II) and Mn(III). The chemistry of manganese in higher states has not been extensively investigated [5]. Some manganese(IV) complexes have been obtained with organic ligands [6] and some oxo-bridged dimanganese(IV) and dimanganese(III, IV) complexes [7].

Ruthenium draws particular attention because it presents the four oxidation portion of the popular $[Ru(bpy)_3]^{+2}$ sensitized photosystem [8]. Ruthenium complexes can form the core of new polymetallic systems that may have applications in excited state energy and electron transfer reactions [9]. The oxo complexes of ruthenium have been shown to act as selective oxidants; polypyridyl complexes of ruthenium electrocatalytically oxidize alcohols, phenols, aldehydes and cyclic ketones, even certain C–H bonds. The ligands, derived by condensation of a primary amine and an active carbonyl groups, contain the azomethine group. They form stable complexes with metal ions especially if the amine or the carbonyl compounds contain a second functional group sufficiently near the site of condensation to form a five or six-membered chelate ring upon complexation [10]. Complexes of *bis*(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone with a variety of transition metals have been reported [11–17]. From our laboratory [18], a template synthesis by reaction of $Mn(OAc)_2 \cdot 4H_2O$, oxaloyldihydrazide and 2-hydroxy-1-naphthaldehyde has been carried out in ethanol. But there is no report on the reaction of preformed *bis*(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone with $Mn(OAc)_2 \cdot 4H_2O$ in methanol under basic conditions. It is reported that the reaction of preformed dihydrazones with manganese(II) chloride in ethanol under reflux in the presence of air gave manganese(II) complexes only. Thus it was thought of interest to examine the reaction of preformed dihydrazone(naohH$_4$) with $Mn(OAc)_2 \cdot 4H_2O$ in methanol under reflux in basic conditions. There is no report on complexes of Ru(III) chloride with the dihydrazone. Keeping in view the importance of manganese and ruthenium complexes, synthesis and characterization of manganese(IV) and ruthenium(III) complexes from polyfunctional bis(2-hydroxy-1-naphthaldehyde)oxa-loyldihydrazone have been investigated in this communication.

2. Experimental

2.1. *Materials*

Manganese(II) acetate tetrahydrate, ruthenium(III) chloride trihydrate, potassium hydroxide, diethyloxalate, hydrazine hydrate and 2-hydroxy-1-naphthaldehyde were GR(E-Merck) or equivalent grade reagents. Reagent grade organic solvents were purified and dried by recommended procedures [19]. Commercial grade ruthenium trichloride was activated by dissolving in concentrated hydrochloric acid and then evaporating to dryness over steam bath before using it for synthesis of complexes.

2.2. *Analysis of the complexes*

Estimation of manganese, ruthenium and chlorine was done following the standard literature procedures [20, 21]. C, H and N were determined microanalytically.

2.3. *Physical measurements*

The molar conductance values of the complexes at 10^{-3} M in DMF solution were measured on a Systronics Direct Reading Conductivity meter-303 with a dip type conductivity cell at room temperature. Magnetic susceptibility measurements were carried out on a Vibrating Sample Magnetometer. Electronic spectra were recorded on a Spectroscan 2600 double beam UV–Vis spectrophotometer (Chemito) and on a Perkin-Elmer Lambda 25 UV–Vis spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer Model spectrum BX-II IR spectrophotometer in the range 4000–450 cm^{-1} in KBr discs and in the range 600–50 cm^{-1} in CsI discs. The ESR spectra of the complexes were recorded at X-band frequency on a Varian E-112E-line century series ESR spectrometer using TCNE ($g = 2.00277$) as an internal field marker. Electrochemical measurements were performed under dry nitrogen with an ECDA-001 Basic Electrochemistry system with 0.1 M tetra-*n*-butyl ammonium perchlorate (TBAP) as the supporting electrolyte and Ag/AgCl as reference electrode.

2.4. *Preparation of ligand*

The *bis*(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone(naohH$_4$) was prepared in two steps. In the first step oxaloyldihydrazine was prepared by the reaction of diethyloxalate (5 mL) and hydrazine hydrate (4.1 mL) in 1 : 2 molar ratio under reflux for 45 min. The product thus isolated was recrystallized from dilute ethanol. In the second step, oxaloyldihydrazine (1.0 g, 8.47 mM) in ethanol (150 mL) solution was allowed to react with 2-hydroxy-1-naphthaldehyde (3.205 g, 18.63 mM) in ethanol (250 mL) over a hot plate at 70 °C with constant gentle stirring for about 30 min and the reaction mixture was refluxed for 2 h. The yellow precipitate so obtained was purified by repeated washing with hot ethanol and finally with ether and dried over anhydrous CaCl$_2$. [Yield: 72%] (m.p. > 300°C). Anal. Calcd for C$_{24}$H$_{18}$N$_4$O$_4$(%): C, 67.60; H, 4.22; N, 13.14. Found: C, 68.00; H, 4.30; N, 13.20. λ_{max} (nm), 259 (7293 dm^{3}mol^{-1}cm^{-1}), 327 (5108 dm^{3}mol^{-1}cm^{-1}), 382 (4231 dm^{3}mol^{-1}cm^{-1}), 435 (600 dm^{3}mol^{-1}cm^{-1}); ν(cm^{-1}) 3530–3300(sbr), 3442(s), 3251(s), 3171(s), (OH + NH); 1699(s), 1690(s)(C=O); 1629(s), 1607(s)(C=N); 1534(s) [amide II(CO + NH) + (C–O)(naptholic)]; 1272(m)[β(C–O)]; 1031(w)(N–N).

2.5. *Preparation of [Mn^{IV}(naoh)(H$_2$O)$_2$] (1)*

To a suspension of *bis*(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone (1.0 g, 2.347 mM in 30 mL methanol) a 30 mL methanolic solution containing Mn(OAc)$_2 \cdot$4H$_2$O (0.556 g, 2.269 mM) was added with vigorous stirring for 45 min which resulted in a dark yellow mixture. To this, KOH (1.018 g, dissolved in 20 mL methanol) was added accompanied by gentle stirring which gave a clear brown solution and any undissolved material was removed by filtration. The solution was stirred for another half an hour which yielded a brown amorphous compound which was filtered, washed with methanol and dried over anhydrous CaCl$_2$. [Yield: 56.3%].

2.6. *Preparation of [Mn^{IV}(naoh)(A)$_2$] [A = py(2), 3-pic(3) or 4-pic(4)]*

These compounds were prepared by following essentially the above method except adding simultaneously pyridine bases to the solution obtained after addition of KOH to the Mn(OAc)$_2$·4H$_2$O and dihydrazone suspension. The brown complexes were isolated in yields of 56–64%.

2.7. *Preparation of [Ru^{III}(naohH$_4$)Cl(H$_2$O)Cl$_2$] (5)*

To a suspension of *bis*(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone (1.64 g, 3.849 mM in 20 mL methanol) a 20 mL methanolic solution of RuCl$_3$·3H$_2$O (1.0 g, 3.82 mM) was added and stirred for 10 min followed by refluxing for 1 h. The color of the reaction mixture was green. It was filtered hot and any undissolved residue was rejected. The filtrate was kept for crystallization precipitating a green compound after 2 days which was filtered, washed with methanol and ether and dried over anhydrous CaCl$_2$. [Yield: 64.3%].

2.8. *Preparation of [Ru^{III}(naohH$_4$)Cl(A)Cl$_2$] [A = py(6), 3-pic(7) or 4-pic(8)]*

These compounds were prepared by following essentially the same procedure as used in preparation of [Ru^{III}(naohH$_4$)Cl(H$_2$O)Cl$_2$] (5) by adding simultaneously pyridine, 3-picoline or 4-picoline to the reaction mixture obtained after addition of dihydrazone to RuCl$_3$·3H$_2$O and refluxing for another half hour. The green complexes were isolated after 2 days in yields of 63.75–65.12%.

3. Results and discussion

Reaction of preformed bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone with Mn(OAc)$_2$·4H$_2$O in methanol under basic condition precipitated Mn(IV) complexes; oxygen probably acts as oxidizing agent. The complexes isolated in the present study, together with their color, decomposition temperature, analytical data, magnetic moment, molar conductance and electronic spectral data are presented in table 1. Tables 2 and 3 include important IR spectral bands of the complexes and ESR spectral data, respectively. The analytical data and stoichiometries of the complexes reveal complexes of compositions [Mn^{IV}(naoh)(A)$_2$] [A=H$_2$O(1), py(2), 3-pic(3) or 4-pic(4)] and [Ru^{III}(naohH$_4$)Cl(A)Cl$_2$] [A=H$_2$O(5), py(6), 3-pic(7) or 4-pic(8)]. The manganese complexes are either brown or dark brown while ruthenium complexes are light green to dark green. All the complexes are air stable, insoluble in water and common organic solvents such as EtOH, MeOH, CH$_3$COCH$_3$, CCl$_4$, CHCl$_3$, Et$_2$O, C$_6$H$_6$, CH$_2$Cl$_2$ and CH$_3$CN, but soluble in DMF and DMSO. The complexes do not decompose to 300°C except **7** and **8** which melt with decomposition at 285 and 272°C, respectively. Weight loss experiments for the complexes were carried out by heating a small amount of sample in glass tube for 4 h in an electric oven maintained at 110, 180 and 220°C. None of the complexes show weight loss at 110°C ruling out the presence of lattice water in

Table 1. Analytical data, magnetic moment, molar conductance and electronic spectral data for monometallic manganese(IV) and ruthenium(III) complexes.

Complex (Color)	% Yield (Dec. Temp °C)	Elemental analysis found (Calcd) (%)					μ_B (B.M)	Λ_M (Ω^{-1} cm^2 mol^{-1})	Electronic spectral bands Λ_{max} (nm) (ε_{max} dm^3 mol^{-1} cm^{-1})
		Mn/Ru	C	H	N	Cl			
Mn^{IV}(naoh)(H$_2$O)$_2$] (**1**) (Dark brown)	56.30 (>300°C)	10.66 (10.72)	55.22 (56.14)	3.41 (3.50)	10.86 (10.91)	–	4.12	10.60	298(1429), 501(2005), 366(1402),
Mn^{IV}(naoh)(py)$_2$] (**2**) (Reddish brown)	56.00 (>300°C)	8.54 (8.66)	65.01 (64.25)	3.75 (3.77)	13.28 (13.22)	–	3.90	10.70	304(2506), 521(3148), 361(2486)
Mn^{IV}(naoh)(3-pic))$_2$] (**3**) (Reddish brown)	58.90 (>300°C)	8.25 (8.29)	64.90 (65.15)	4.25 (4.22)	12.55 (12.66)	–	3.93	10.00	286(2257), 342(2077), 322(2176), 394(2023), 462(2401)
Mn^{IV}(naoh)(4-pic)$_2$] (**4**) (Reddish brown)	64.00 (>300°C)	8.16 (8.29)	65.10 (65.15)	3.90 (4.22)	12.60 (12.66)	–	3.90	10.50	292(2790), 360(3690), 311(3069), 466(6010)
Ru^{III}(naohH$_4$)Cl(H$_2$O)Cl$_2$] (**5**) (Dark green)	64.20 (>300°C)	15.55 (15.50)	44.22 (44.20)	3.05 (3.06)	8.54 (8.59)	16.38 (16.34)	1.69	6.40	298(1413), 489(1978), 362(1424), 651(3150)
Ru^{III}(naohH$_4$)Cl(py)Cl$_2$] (**6**) (Dark green)	64.30 (>300°C)	14.06 (14.17)	48.90 (48.84)	3.20 (3.22)	9.79 (9.82)	15.00 (14.94)	1.70	9.70	276(4635), 406(1708), 310(8930), 654(830)
Ru^{III}(naohH$_4$)Cl(3-pic)Cl$_2$] (**7**) (Dark green)	65.12 (>285°C)	13.85 (13.90)	49.72 (49.55)	3.42 (3.44)	9.64 (9.63)	14.60 (14.65)	1.65	9.50	406(1720), 656(175), 469(790)
Ru^{III}(naohH$_4$)Cl(4-pic)Cl$_2$] (**8**) (Light green)	63.75 (>272°C)	13.80 (13.90)	49.72 (49.55)	3.40 (3.44)	9.70 (9.63)	14.66 (14.65)	1.64	10.00	302(3700), 501(1086), 366(3840), 606(1070)

Table 2. Characteristic IR bands (cm^{-1}) for manganese(IV) and ruthenium(III) complexes.

Complex	ν(OH) + ν(NH)	ν(C=O)	ν(C=N)	AmideII + ν(C–O) (naphtholic)	ν(NCO)	β(C–O)	ν(M–O)	ν(N–N)
[Mn^{IV}(naoh)(H$_2$O)$_2$]	3600–3000(vsbr) 3400(s)	–	1617(s) 1598(s)	1534(vs)	1534(vs)	1298(m)	558(msh)	1033(w)
[Mn^{IV}(naoh)(py)$_2$]	3600–3000(vsbr) 3457(s)	–	1622(s)	1544(s)	1544(s)	1309(m)	542(msh)	1042(w)
[Mn^{IV}(naoh)(3-pic)$_2$]	3600–3000(sbr) 3448(s)	–	1619(s) 1592(s)	1542(s)	1544(s)	1319(m)	584(m)	1032(w)
[Mn^{IV}(naoh)(4-pic)$_2$]	3600–3000(sbr) 3468(s)	–	1635(s)	1540(s)	1540(m)	1319(w)	–	–
[Ru^{III}(naohH$_4$)Cl(H$_2$O)Cl$_2$]	3600–3300(sbr) 3476(s)	1680(s)	1616(s) 1593(s)	1547(s)	–	1285(m)	558(m)	1035(w)
[Ru^{III}(naohH$_4$)Cl(py)Cl$_2$]	3600–3350(sbr) 3339(s) 3251(s) 3159(s)	1678(s)	1622(s) 1599(s)	1530(s)	–	1282(m)	551(msh)	1074(w)
[Ru^{III}(naohH$_4$)Cl(3-pic)Cl$_2$]	3445(s) 3163(s)	1677(s)	1621(s) 1592(ssh)	1530(s)	–	1318(m)	546(wsh)	1032(w)
[Ru^{III}(naohH$_4$)Cl(4-pic)Cl$_2$]	3432(s) 3170(s)	1677(s)	1612(s) 1600(s)	1535(w)	–	1282(w)	582(w)	1035(W)

Table 3. ESR parameters of monometallic manganese(IV) and ruthenium(III) complexes derived from $naohH_4$.

Complex	g-values		g-values (LNT DMF)			
	(RT powder)	(LNT powder)	$g_\parallel$	$g_\perp$	g_{av}	A(G)
$[Mn^{IV}(naoh)(H_2O)_2]$ (1)	4.644	3.824	–	–	–	[55]Mn 100
	2.031	2.019				
$[Mn^{IV}(naoh)(py)_2]$ (2)	4.334	4.334	–	–	–	100
	2.019	2.019				100
$[Mn^{IV}(naoh)(3\text{-}pic)_2]$ (3)	4.334	4.334	–	–	–	100
	2.012	2.012				100
$[Mn^{IV}(naoh)(4\text{-}pic)_2]$ (4)	4.645	4.646	–	–	–	100
	2.044	2.044				100
$[Ru^{III}(naohH_4)Cl(H_2O)Cl_2]$ (5)	–	2.196	2.408	1.982	2.266	[101]Ru 96
$[Ru^{III}(naohH_4)Cl(3\text{-}pic)Cl_2]$ (7)	–	2.190	2.481	2.110	2.357	–
$[Ru^{III}(naohH_4)Cl(4\text{-}pic)Cl_2]$ (8)	–	2.500	2.580	1.912	2.357	–

their structure. But, **1** and **5** show weight loss corresponding to one water at 180 °C suggesting coordinated water. The water molecules were identified by passing the issuing vapors through a trap containing anhydrous $CuSO_4$ which turned blue. Complexes (**2–4**) and (**6–8**) show weight loss at 220°C corresponding to pyridine, 3-picoline or 4-picoline. The vapors evolved at this temperature turned a solution of $CHCl_3$ containing a drop of 5M NaOH solution red confirming that they originated from pyridine bases [22]. The expulsion of these donor molecules at such a high temperature indicates that they are coordinated to the metal center.

3.1. *Molar conductance*

Molar conductance values in the range 6.40–10.70 $\Omega^{-1}cm^2mol^{-1}$ for the complexes in DMF at 10^{-3} M are consistent with non-electrolytes [23].

3.2. *Magnetic moment*

The manganese complexes (**1–4**) have μ_B in the range 3.90–4.12 B.M. consistent with manganese(IV) complexes in a d^3 high-spin electronic configuration ($S = 3/2$) [24, 25]. The μ_B value for the monometallic ruthenium complexes (**5–8**) are in the range 1.64–1.70 B.M. suggesting one unpaired electron indicating +3 oxidation state for ruthenium in these complexes (low spin d^5, $S = 1/2$) [26].

3.3. *Electronic spectra*

The free ligand ($naohH_4$) shows four bands at 259(7293), 327(5108), 382(4231) and 435(600) nm in DMF. The bands in the region 259–382 nm are assigned to intra ligand $n-\pi^*$ and $\pi-\pi^*$ transitions. The band at 382 nm is characteristic of naphthaldimine as reported in several mono acylhydrazones while the band at 435 nm arises due to a forbidden transition in dihydrazone. The ligand bands 327 and 382 nm show fine

structure due to vibronic coupling [27]. The electronic spectra of (**1–4**) show the intra ligand transitions and a band in the region 462–521 nm. For octahedral manganese(IV) complexes three spin-allowed d–d transitions $^4A_{2g} \rightarrow {}^4T_{2g}$, $^4A_{2g} \rightarrow {}^4T_{1g}(F)$ and $^4A_{2g} \rightarrow {}^4T_{1g}(p)$ are expected. The manganese(IV) complex, $[MnF_6]^{2-}$, shows two absorption bands at 360 and 450 nm assignable to $^4A_{2g} \rightarrow {}^4T_{1g}(F)$ and $^4A_{2g} \rightarrow {}^4T_{2g}$, respectively [28, 29], while the third band arising due to $^4A_{2g} \rightarrow {}^4T_{1g}(p)$ is obscured either by charge transfer or ligand bands. The d–d absorption bands in the present study cannot be identified as they are obscured by charge transfer or ligand bands. The additional bands found in the region 462–521 nm cannot be assigned to spin-allowed d–d transitions because their absorption coefficients lie in the range 20050–24010 $dm^3 mol^{-1} cm^{-1}$. These bands are assigned to charge-transfer bands, probably from the naphtholate (oxygen) to the d-orbital of the manganese(IV).

Complexes (**5–8**) show either one or two bands in the region 469–656 nm in addition to the ligand bands. The bands from 469–501 nm are assigned to charge transfer from ligand to metal (LMCT) in view of their high molar extinction coefficient values. However, the bands in the region 469–656 nm are assigned to d–d transitions. This band in **5** and **6** may have contribution from adjacent charge transfer band as well as it has high molar extinction. The band in the 620–645 nm region has been assigned to the spin allowed $^1A_{1g} \rightarrow {}^1T_{1g}$ transition [30]. The other high intensity bands in the region 400–440 nm were assigned to charge transfer or intraligand transitions [31].

3.4. *Infrared spectra*

The IR spectrum of the ligand is complicated due to a large number of groups which have overlapping regions. However, a few bands have been selected in order to observe effect of complexation. The structurally significant IR bands for the free dihydrazone and the monometallic complexes are listed in table 2. A comparison of the IR spectra of the complexes with that of naohH$_4$ suggests that the dihydrazone is coordinated to the metal center in enol form in the manganese complexes while in keto form in ruthenium complexes.

The uncoordinated ligand shows a strong broad band in the region 3550–3300 cm^{-1} with its center at 3442 cm^{-1} and two rather intense strong bands at 3251 and 3171 cm^{-1}, which are assigned to $\nu(OH)$ of 2-hydroxy-1-naphthaldehyde part of the dihydrazone and –NH group, respectively.

IR spectra of (**1–4**) show a very strong broad band at 3000–3600 cm^{-1} with centers at 3400–3468 cm^{-1}. The IR spectra of the complexes do not show any band which may be assigned to stretching vibrations of secondary –NH groups, suggesting collapse of amide structure of the ligand in the complexes. The strong broad band in this region might be due to $\nu(OH)$ vibration to either lattice or coordinated water molecule or due to $\nu(OH)$ of moisture absorbed by KBr during pellet preparation. In order to decide upon whether the bands in this region arise due to H_2O molecules or due to moisture absorbed by KBr pellets, the compounds were heated at 110°C and 180°C, respectively. The ensuing vapors were passed through a trap containing anhydrous $CuSO_4$. Complexes **2–4** and **6–8** showed no weight loss due to lattice or coordinated water. This indicates that in these complexes, the bands in the region 3411–3436 cm^{-1} arise due to moisture absorbed by KBr pellets. On the other hand, complex **1** showed weight loss

corresponding to two water molecules at 180°C suggesting that the 3000–3600 cm^{-1} band has contribution due to ν(OH) of coordinated water.

The ν(C=O) bands at 1699 and 1685 cm^{-1} in the free dihydrazone are absent in the IR spectra of the manganese complexes, further suggesting collapse of amide structure of dihydrazone and coordination in the enol form.

Ruthenium complexes (**5–8**) show two to three strong bands in the region 3339–3476 and 3159–3251 cm^{-1}. The essential features of the 3339–3476 cm^{-1} band in these complexes suggest that it is the stretching vibration of –OH from the naphtholic group. The 3159–3251 cm^{-1} bands arise due to stretching of >NH of the coordinated ligand. Such a feature in the IR spectra of the ruthenium complexes in the region 3000–3500 cm^{-1} suggests that the ligand coordinates as a neutral ligand in the keto form. This is confirmed by strong bands in the 1677–1680 cm^{-1} region corresponding to ν(C=O) which appear at 1699 and 1685 cm^{-1} in the free dihydrazone. This band shows a shift of about 12–15 cm^{-1} in these complexes but still falls in the region for uncoordinated >C=O in dihydrazone [32]. This band rules out the possibility of coordination of >C=O to the metal.

The free dihydrazone shows a strong band at 1534 cm^{-1} with composite character due to mixed contribution of the amide-II and ν(CO) (naphtholic) bands. In all of the complexes a medium to strong band appears in the region 1534–1544 cm^{-1}. The position of this band is consistent with the occurrence of bonding through naphtholate oxygen atoms. However, the intensity of the band in this region is considerably increased in **1–4** suggesting contribution from the NCO$^-$ group [33] produced as a result of enolization of the ligand.

The ligand shows two very strong bands at 1629 and 1607 cm^{-1} assigned to stretching vibration of azomethine [29, 34–41]. The average position of the ν(C=N) bands shifts to lower frequency by 7 to 12 cm^{-1} in all of the complexes of ruthenium but not in the complexes of manganese. This indicates bonding between azomethine nitrogen and ruthenium. The ν(C=N) stretching vibration shifts to higher frequency in **2** and **4** at 1622 and 1635 cm^{-1}, respectively. The ν(C=N) stretching vibration in the form of two bands in the IR spectra of the complexes similar to that in the dihydrazone indicates that the two >C=N groups are inequivalent, suggesting that the two azomethine nitrogen-to-metal bonds are unequal. Such an inequivalency in the strength of the M←N bonds may be related to coordination of dihydrazone to the metal centre in the *anti-cis*-configuration. In this configuration, one hydrazone attains axial position while the other hydrazone remains in the equatorial position [42].

In the dihydrazone a medium intensity band at 1272 cm^{-1} is similar to other ligands containing phenol. Hence, this band is assigned to β(C–O) (naphtholic) [43]. This band is shifted to higher frequency in the complexes by 10–47 cm^{-1}, indicating bonding to metal through naphtholate oxygen.

Manganese complexes (**2–4**) and ruthenium complexes (**6–8**) show a band in the region 1072–1105 cm^{-1}, assigned to ring breathing of pyridine, 3-picoline or 4-picoline in the complexes. This band indicates coordination of pyridine, 3-picoline or 4-picoline, molecule(s) to the metal center [44]. Complexes **2–4** and **6–8** show weight loss corresponding to two molecules of pyridine, 3-picoline or 4-picoline and one molecule of pyridine, 3-picoline or 4-picoline at 220 °C suggesting that they are coordinated to the metal centers.

The region below $600\,cm^{-1}$ is very complicated and several weak bands in addition to those observed in the ligand are observed in the resulting complexes obviously due to the splitting of skeletal vibrations. From the infrared spectral data discussed above, it is evident that the ligand binds to metal through naphtholate oxygen and hydrazide nitrogen either in the keto form or enol form. The ν(M–O) (naphtholic) [45–47] may be expected at higher frequencies than ν(M–O) (carbonyl) [48, 49] for difference in bond order. On examining the spectra of the ligands and its manganese and ruthenium complexes below $600\,cm^{-1}$, the new band appearing in the 542–$584\,cm^{-1}$ region is tentatively assigned to ν(M–O)(naphtholate).

3.5. *ESR spectra*

The ESR parameters for the complexes are provided in table 3.

The manganese(IV) complexes in the polycrystalline phase at RT and LNT show almost twinlar features. Two resonances are observed, a strong one near $g = 2.00$ and weak one near $g = 4.00$. At RT the ^{55}Mn hyperfine structure is weakly resolved for all the complexes, except **1**, for the resonance near $g = 2.00$. However, the hyperfine structure is well resolved for all the complexes at LNT.

In crystal field of strict octahedral symmetry, a d^3 ion has $^4A_{2g}$ ground state leading to an isotropic resonance at $g = 2.0$ [50]. Distortion and spin-orbit coupling split the ground state quartet into two Kramer's doublets separated by $2(D^2 + E^2)$ where D and E are axial and rhombic zero field splitting parameters, respectively. The complexity of an ESR spectra of a d^3 ion in an axial field ($E/D = 0$) is dependent on the magnitude of zero field splitting parameters [51, 52]. Two limiting cases are when the value of axial zero field splitting parameters, 2D, is either much larger or much smaller than $h\nu$ ($0.31\,cm^{-1}$ at X-band frequencies). In the first case, the feature at low field is strong and the $g = 2.0$ component is weak. This is the observation for *tris*(catacholato)manganese(IV) [53] and *tris*(sorbitolato)manganese(IV) complexes [54]. When D is small, the $g = 2.0$ component should dominate with relatively weak signals in the low field region. Such features have been observed for tris(thiohydroxamato)manganese(IV) [55] and *tris*(dithiocarbamato)manganese(IV) complexes [56]. The spectral features observed in the present study (strong $g = 2.0$) and (weak $g = 4.0$ resonances) are characteristic of small axial distortion, $2D \ll h\nu$. Interestingly, the ^{55}Mn hyperfine coupling constant for the $g = 2.00$ signal lies in the region 94–100G which is close to 100G for known $2D \ll h\nu$ for the species.

The g values for the manganese(IV) complexes do not change on lowering the temperature except complex **1**. This shows that the structure of **1** changes at lower temperature but not in the remaining complexes. This may be attributed to strong donor character of pyridine ring in **2–4** as compared to that of water in **1**.

The ESR spectra of the low-spin ruthenium(III) complexes **5**, **7** and **8** were recorded as a polycrystalline solid at RT and LNT and in DMF solution at RT and LNT. The room temperature ESR spectra of the complexes were featureless. The ESR spectra of the complexes at LNT in polycrystalline state do not show hyperfine splitting but consist of a single isotropic resonance. The ESR spectra of the complexes in DMF solution at LNT show two resolved signals corresponding to $g_\parallel$ and $g_\perp$ and in each case $g_\parallel > g_\perp$. Only **5** shows hyperfine splitting in perpendicular region with hyperfine splitting constant equal to 96G.

3.6. *Cyclic voltammetry*

The cyclic voltammetry studies of the complexes, $[Mn^{IV}(naoh)(H_2O)_2]$ (**1**) and $[Ru^{III}(naohH_4)Cl(3-pic)Cl_2]$ (**7**) were done in DMF solution in nitrogen at the scan rate of $100\,mV\,s^{-1}$ with Ag/AgCl reference electrode, as representative examples. The voltammogram of $[Mn^{IV}(naoh)(H_2O)_2]$ showed two oxidation and two reduction peaks, presumably Mn^{IV}–Mn^{III} and Mn^{III}–Mn^{II} couples. The Mn^{IV} complex shows two waves with peaks (*vs.* Ag/AgCl reference electrode) at $E_{1/2} = 0.687V$ ($E_{pc} = 0.331V$, $E_{pa} = 1.034V$) and at $E_{1/2} = 0.072V$ ($E_{pc} = -0.091V$, $E_{pa} = 0.237V$) for Mn^{III}–Mn^{II} quasi-reversible redox process which was judged from the peak-current ratios. In addition to these two waves, the complex shows a reductive wave at $-1.148V$ which is assumed to be associated with the reduction of coordinated dihydrazone ligand. The highest peak separation might originate from a slow heterogeneous electron-exchange rather than an interfering homogeneous reaction [57].

The voltammogram of $[Ru^{III}(naohH_4)Cl(3-pic)Cl_2]$ showed an oxidation and a reduction with $E_{1/2} = -0.206\,V$ (*vs.* Ag/AgCl reference electrode) ($\Delta E_{peak} = 110\,mV$), suggesting Ru^{III}–Ru^{II} couple. Another oxidation and reduction at $-0.550V$ and $-1.120\,V$, respectively, is observed, which may presumably be associated with the dihydrazone ligand.

4. Conclusions

The stoichiometries of manganese(IV) complexes obtained by the reaction of preformed *bis*(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone in methanol under
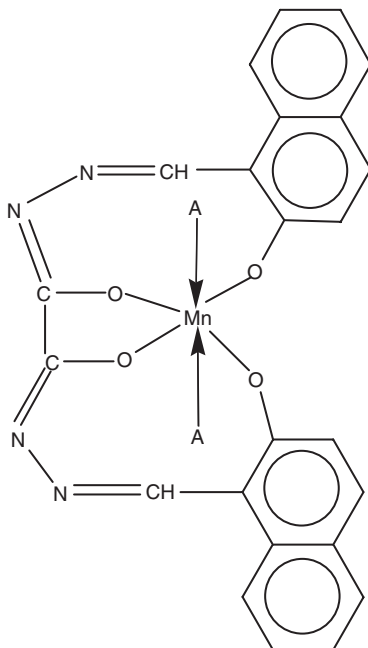

Figure 1. Suggested structure of $[Mn^{IV}(naoh)A_2]$ [where $A = H_2O(\mathbf{1})$, py(**2**), 3-pic(**3**) and 4-pic(**4**)].
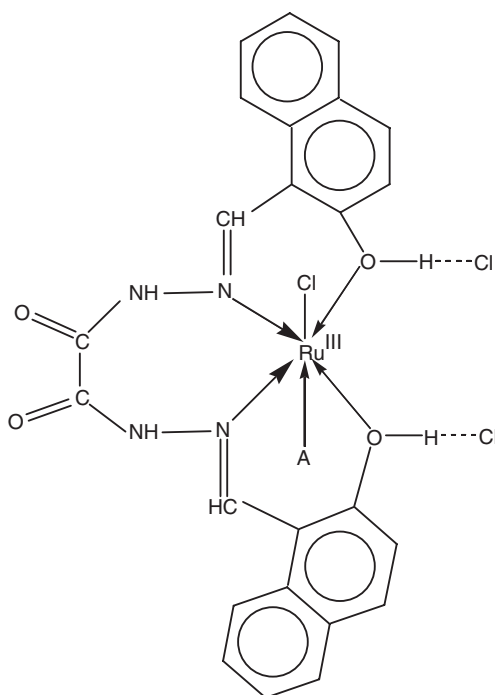
Figure 2. Suggested structure of $[Ru^{III}(naohH_4)Cl(A)Cl_2]$ [where $A = H_2O$(**5**), py(**6**), 3-pic(**7**) and 4-pic(**8**)].

basic conditions are more or less similar to those obtained by template synthesis except for lattice water molecules. But from IR spectral studies, it is clear that preformed dihydrazone under basic conditions is tetradentate, coordinating to Mn(IV) in enol-form while in the template synthesis dihydrazone coordinates tetradentate in the keto-form. Preformed dihydrazone coordinates to Ru(III) in the keto-form. Based on analytical data and physico-chemical studies, octahedral stereochemistry around metal ions have been proposed. The proposed tentative structures of these complexes are shown in figures 1 and 2.

Acknowledgements

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